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International application number: PCT/CA05/000406

International filing date: 16 March 2005 (16.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 60/553,121  
Filing date: 16 March 2004 (16.03.2004)

Date of receipt at the International Bureau: 27 April 2005 (27.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in  
compliance with Rule 17.1(a) or (b)



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FILING DATE UNDER 35 USC 111.**

**APPLICATION NUMBER: 60/553,121**

**FILING DATE: March 16, 2004**

*PCT/CA05/00406*

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13281 U.S. PTO

## PROVISIONAL APPLICATION COVER SHEET

To the Commissioner of Patents and Trademarks  
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This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(b)(2).

Docket No.	14648PRO	Type a plus sign (+) inside this box -	+
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TITLE OF THE INVENTION (280 characters max)

HYBRID ORGANIC-INORGANIC MESOPOROUS MATERIALS

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STATE	Virginia	ZIP CODE	22202	COUNTRY	United States
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ENCLOSED APPLICATION PARTS (check all that apply)

<input checked="" type="checkbox"/> Specification	Number of Pages	40	<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets	7
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METHOD OF PAYMENT (check one)

<input checked="" type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees	Provisional filing fee amount(s)	\$ 80.00
<input checked="" type="checkbox"/> Applicant(s) claim small entity status		
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees and credit any overages to Deposit Account Number: 04-1577		

Respectfully submitted,

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60/553121

031604

**UNITED STATES PROVISIONAL APPLICATION**

**Title: HYBRID ORGANIC-INORGANIC MESOPOROUS MATERIALS**

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## HYBRID ORGANIC-INORGANIC MESOPOROUS MATERIALS

### FIELD OF THE INVENTION

5 The present invention relates to new composite materials, called hybrid organic-inorganic mesoporous materials, a new class of mesoporous materials whose properties can be easily tuned through organic chemistry to fit a desired application by introducing functional molecules carrying organic, organometallic or biological groups exclusively on the surfaces of the channel pores of a pre-existing mesoporous framework. The high porosity and surface area, as well as  
10 the controllable properties due to the presence of functional organic, organometallic or biological groups exclusively on the surfaces of these materials make them ideal candidates for use in applications such as microelectronics, catalysis, sensors, chromatography, drug delivery and bioassays.

15

### BACKGROUND OF THE INVENTION

Periodic mesoporous silica materials denoted M41S or MCM-type having pore sizes 2-10 nm were first disclosed in Kresge, C. T.; Leonowicz, M.; Roth, W. J.; Vartuli, J. C.; Beck, J. C. **Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism**, *Nature*, 359, 710  
20 (1992). Their discovery represented a paradigm shift in the synthesis of porous inorganic materials with a structure founded upon a regular array of monodispersed pores in the mesoscale size range of 2-30 nm defined by the



International Union of Pure and Applied Chemistry IUPAC convention for porous solids.

To amplify, the materials were prepared in a straightforward synthesis that involved the aqueous phase co-assembly and acid or base catalyzed hydrolytic poly-condensation of silicate-surfactant micelles followed by removal of the surfactant by thermal or chemical or photochemical post-treatment steps. This synthesis strategy created a silica replica of the templating micelles (a silicotropic mesophase) and represented a new way of creating silica materials with crystalline mesoporosity having a pore architecture (e.g., hexagonal, cubic, worm-hole) and pore dimensions (range of diameters 2-10 nm) that were predicated upon the structure and dimensions of the surfactant-directing micelle assembly. Using this synthetic approach the mesopore dimensions could be chemically controlled with angstrom precision anywhere in the range of 2-10 nm. In a creative extension of this strategy, researchers at the University of California at Santa Barbara demonstrated that by using tri-block copolymer micelles, involving for example the co-assembly of a polypropylene oxide-polyethylene oxide-polypropylene oxide mesophase with silicate precursors, as a new and larger dimension templating mesophase, then the mesopore size range of the MCM41 class of periodic mesoporous silica materials could be boosted to the upper mesoscale range of 10-30 nm to create a new class of much larger mesopore silica materials that were denoted SBA periodic mesoporous silicas, see Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. **Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly**

ordered, hydrothermally stable, mesoporous silica structures, *J. Am. Chem. Soc.*, 120, 6024 (1998).

5 It is important to note that the channel walls of all of these MCM and SBA  
classes and structure types of periodic mesoporous silicas were glassy having  
just short range order, the channel walls lacked structurally well defined silica  
sites like those found in zeolites, and were found to be devoid of useful channel  
functionality for perceived applications that could benefit from the size and shape  
controlled mesopores of the materials. In other words while the mesopores in  
MCM41, MC48 and SBA materials were monodispersed (single size) and the  
10 mesoporosity could be either periodic (hexagonal, cubic) or randomly organized  
(worm hole - see Linssen, T.; Cassiers, K.; Cool, P.; Vansant, E. F. **Mesoporous  
templated silicates: an overview of their synthesis, catalytic activation and  
evaluation of the stability**, *Advances in Colloid and Interface Science*, 103, 121  
(2003)), the material behaved more or less like any other form of porous silica  
15 derived from say silica sol-gel type chemistry, exemplified by well-known classes  
of materials called xerogels and aerogels, and that contained a random spatial  
distribution of different diameter mesopores in a glassy silica matrix. Hence the  
envisioned benefits of this new class of periodic mesoporous silica MCM41,  
MC48 and SBA materials were never really realized in practice and to the best of  
20 our knowledge no products or processes have emerged in the more than ten  
years since their discovery.

Since their discovery, tremendous efforts have been devoted to overcome  
the functionality deficiency of the MCM41, MC48 and SBA class of mesoporous

silica materials by, for example, incorporating other elements into the materials, creating entirely different compositions, crystallizing the constituents of the channel walls, and of special relevance to the present invention, by incorporating useful organic functionality into the materials, see - Asefa, T.; Ozin, G. A.;

5 Grondey, H.; Kruk, M.; Jaroniec, M. **Recent developments in the synthesis and chemistry of periodic mesoporous organosilicas**, *Studies in Surface Science and Catalysis*, 141, 1 (2002). In the context of the latter direction of investigation, two main methods of building organic function into periodic mesoporous silica to create periodic mesoporous organosilica have been

10 devised. The first involving a three--step process based upon first synthesizing by template directed means a periodic mesoporous silica, second removing said template from the as-synthesized periodic mesoporous silica and third grafting organo-functionalized alkoxysilanes  $\text{RSi}(\text{OEt})_3$  to channel surface silanol groups  $\text{SiOH}$  to give the desired periodic mesoporous organosilica. In the second

15 approach, instead of a three-step process a one-step method is utilized to obtain the desired periodic mesoporous organosilica that involves co-assembly of organo-functionalized alkoxysilanes  $\text{RSi}(\text{OEt})_3$  with alkoxysilanes  $\text{Si}(\text{OEt})_4$ , see - Asefa, T.; Ozin, G. A.; Grondey, H.; Kruk, M.; Jaroniec, M.. **Recent**

20 **developments in the synthesis and chemistry of periodic mesoporous organosilicas**, *Studies in Surface Science and Catalysis*, 141, 1 (2002). The organic groups utilized in the precursors  $\text{RSi}(\text{OEt})_3$  used for both of these synthetic approaches, which ends up in the desired periodic mesoporous organosilica product is terminally bound to the silicon atom in said precursors



and said product. Whichever synthetic strategy is used to make these periodic mesoporous organosilicas with organic groups terminally bound to the walls of the pores the surfactant template can be removed from the material by thermal or chemical or photochemical post-treatment steps. In this context of template removal from said as-synthesized periodic mesoporous organosilica, thermal usually means heating in air or oxygen to oxidatively remove said template from said as-synthesized periodic mesoporous silica under conditions that do not destroy said terminal organic function, photochemical usually means irradiating said template containing periodic mesoporous silica with ultraviolet light in air or oxygen to photooxidatively remove said template from said as-synthesized periodic mesoporous silica under irradiation conditions that do not destroy said terminal organic function, chemical usually means reacting said template containing periodic mesoporous silica with a reagent that serves to chemically remove said template from said as-synthesized periodic mesoporous silica under irradiation conditions that do not destroy said terminal organic function.

Another way of incorporating this kind of terminally bound organic functionality to the pore walls of the periodic mesoporous silica is a modification of the three-step grafting procedure described above but is instead reduced to a two-step process by circumventing the template removal step. This is achieved by adding the organo-functionalized alkoxysilane  $\text{RSi}(\text{OEt})_3$  directly to the as-synthesized template-containing periodic mesoporous organosilica whereby it is able to simultaneously displace the imbibed template from the periodic mesoporous silica and thereby anchor to silanol groups on the pore wall of the periodic

mesoporous silica as a terminally bound organic group through a single chemical linkages, Yi-Hsin Liu, Hong-Ping Lin, and Chung-Yuan Mou, **Direct Method for Surface Silyl Functionalization of Mesoporous Silica**, *Langmuir*, (2004); Antochshuk, Valentyn; Jaroniec, Mietek, **Simultaneous Modification of Mesopores and Extraction of Template Molecules from MCM-41 with Trialkylchlorosilanes**, *Chemical Communications*, 23, 2373 (1999).

To emphasize, in all three cases mentioned above the desired organic function in the resulting periodic mesoporous organosilica material is chemically bound to the surface of the channel walls as a terminal organic group through a single chemical linkage and protrudes into the channel and hence to some extent occupies channel void space and also serves to block the passage of guests in the channels. Moreover the distribution of organic functional groups within the channels is not strictly under control and effects of localized anchoring in the pore mouths of the mesopores and phase separation of precursors results in inhomogeneous patterns of organic groups on the surface of the channel walls.

A creative and inventive way to circumvent all of these problems with surface attached terminal organic groups on the channel walls of periodic mesoporous organosilicas was reported simultaneously and independently by three research groups at the University of Toronto, see - Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. **Periodic mesoporous organosilicas with organic groups inside the channel walls**, *Nature*, 402, 867 (1999); the University of Minnesota, see Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A., **Mesoporous sieves with unified hybrid inorganic/organic frameworks**,

*Chemistry of Materials*, 11, 3302 (1999); and Toyota Research Laboratories in 1999, see - Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T, Terasaki, O. **Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks**, *Journal of the American Chemical Society*, 121, 9611 (1999). Toyota corporation obtained a patent on this class of periodic mesoporous organosilica materials - Inagaki, Shinji; Guan, Shiyou; Fukushima, Yoshiaki. **Organic/inorganic materials including complexes of porous materials**. Ger. Offen. (2000), DE 19930944.

It involved the use of a new type of silica precursor in the surfactant templated co-assembly process, called silsesquioxanes exemplified by  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$ , in which the organic function R instead of being present as a terminally bonded group to the alkoxysilane as referred to above is rather positioned as a bridging group between two alkoxysilane groups. The resulting templated material is called a periodic mesoporous organosilica (PMO) in which the bridging organic group R is exclusively integrated into the silica framework to create organosilica channel walls. This represents a distinct situation to the earlier generation of mesoporous organosilicate materials mentioned above in which the organic groups are exclusively terminally bound to the surface of silica channel walls and protrude into the channel spaces. In the PMOs by contrast, the mesopores exist in an organosilica matrix built entirely from bridging  $\text{OSiRSiO}$  moieties. Furthermore, by performing the same kind of template directed synthesis but instead using a controlled ratio of the silsequioxane and alkoxysilane precursors in the co-assembly process, it proved possible to access

an entire family of PMO materials in which the loading of the bridging organic group in the organosilica channel walls can be varied between 100% and 0%. In this way it proved feasible to fine-tune the chemical and physical, mechanical and electrical, optical and electronic properties of the PMOs anywhere between the two end members with high fidelity. Other extensions involved the synthesis of novel classes of PMOs containing two or more distinct types of bridging organic groups or indeed PMOs with both bridging and terminal organic groups, see - Asefa, T.; Kruk, M.; MacLachlan, M. J.; Coombs, N.; Grondey, H.; Jaroniec, M.; Ozin, G. A., **Novel bifunctional periodic mesoporous organosilicas, BPMOs: synthesis, characterization, properties and in-situ selective hydroboration-alcoholysis reactions of functional groups**, *Journal of the American Chemical Society*, 123, 8520 (2001).

Still other extensions involved the use of  $[(\text{EtO})_3\text{Si}]_n\text{R}$  silsesquioxane precursors in which  $n = 2,3,4$  to yield PMOs in which the bridging organic group spanning the alkoxysilane groups can be doubly, triply or quadruply bonded and the organic content has been boosted to higher and higher levels, see - Kuroki, M.; Asefa, T.; Whitnal, W.; Kruk, M.; Yoshina-Ishii, C.; Jaroniec, M.; Ozin, G. A. **Synthesis and properties of 1,3,5-benzene periodic mesoporous organosilica (PMO): novel aromatic PMO with three point attachments and unique thermal transformations**, *Journal of the American Chemical Society*, 124, 13886 (2002).

All of these breakthroughs essentially relegated the MCM and SBA classes of periodic mesoporous silica materials, which were devoid of useful

functionality, to be the pure silica end-members of an enormous family of PMOs brimming with valuable functionality that could be orchestrated synthetically through the choice of the bridging organic group R to target a particular application.

5           The ability to directly include, in a predetermined fashion, bridging organic groups into the silica walls of a periodic mesoporous silica created an entirely new class of PMO nanocomposites, synthesized from the "*bottom-up*" and with "*molecular scale*" control, and which offered a myriad of envisioned opportunities based upon the ability to utilize organic synthetic chemistry to control the  
10 chemical and physical properties of the material.

          The trend setting reports of the PMOs from the three inventor groups nevertheless inspired groups around the world to get involved in the materials and extend the research. Hundreds of papers have now appeared on PMOs and are beginning to demonstrate that diverse kinds of organic functionality can be  
15 incorporated into the materials, which can likely be exploited to advantage in a number of application areas including but not limited to catalysis and separations, chemical sensing, bioassays and controlled release of chemicals, microelectronic packaging and digital printing.

          There are, however, some serious deficiencies with the PMOs that are  
20 problematical with respect to a number of perceived areas of application earmarked for the PMOs. These include the fact that a significant fraction of the bridging organic groups are buried within the internal regions of the organosilica channel walls and are therefore not able to be exploited in a number of



applications that require them to be spatially accessible on the surface of the channel walls. These so-called inaccessible organics are essentially wasted in a chemical sense and serve only to make the cost of production of the PMO materials higher than it would have been had they not existed. Another problem concerns the geometric and steric constraints imposed on the bridging organic groups that are accessible on the channel wall surface of the PMO but not necessarily optimally aligned to exploit for example its adsorption and reactivity properties. Also, not all  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane precursors are able to successfully assemble into PMO materials because of either competing and unwanted intramolecular cyclization reactions, unfavorable hydrolytic polycondensation kinetics or collapse of the resulting PMO because the bridging organic group is insufficiently rigid to support the desired mesostructure.

It would be very advantageous to provide a method of producing an entirely new class of hybrid organic-inorganic mesoporous materials that have all the desired attributes of the PMOs but are able to overcome deficiencies of the type mentioned but not limited by the ones mentioned above.

### SUMMARY OF THE INVENTION

An objective of the present invention is to provide a new class of hybrid organic-inorganic mesoporous materials that have at least some of the desired attributes of the PMOs but are able to overcome deficiencies of the PMO materials.

In brief, a straightforward methodology has been developed that exclusively locates a desired bridging organic group just on the surface of the channel walls of, for example, a pre-existing periodic mesoporous silica PMS (MCM41, MCM48 or SBA type material) or periodic mesoporous organosilica (PMO) to create a novel kind of PMO that we denote a hybrid periodic mesoporous organosilica (HPMO). The elegance of this invention is the simplicity of the underlying concept, namely a  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane precursor is chemically anchored to the silanol groups located on the channel surface of a pre-existing mesoporous silica in a very simple one step reaction. It is akin to "painting" the desired  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane organic functionality onto the channel walls of a periodic mesoporous silica, that is the organic is placed just on the surface of the channel wall where it is wanted and none are hidden inside the channel wall where they are unavailable for use.

Because the periodic mesoporous silica framework material (MCM41, MCM48 or SBA type material) pre-exists and is thermally and chemically stable, it has been established in this invention that this material is a useful starting material to successfully anchor all  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane precursors that can be synthesized to the surface silanol groups of the silica channel walls. In this case, as none of the precursors fail to anchor and form a an organosilica framework, this overcomes all of the deficiencies delineated above for the lack of formation of many PMOs because of self-assembly problems associated with intramolecular cyclization and flexibility of the  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane precursors or the instability of the resulting PMOs. A simple extension of this

work is to anchor the  $(\text{EtO})_3\text{SiRSi}(\text{OEt})_3$  silsesquioxane precursors on the surface of a pre-existing PMO. In this way one can have one kind of bridging organic group within the channel walls and another type on the surface of the channel walls, thereby facilitating independent control of the chemical and physical properties of the HPMOs. Another extension is to use  $[(\text{EtO})_3\text{Si}]_n\text{R}$  silsesquioxane precursors with  $n = 2, 3, 4$  in which the bridging organic group spanning the alkoxysilane groups can be doubly, triply or quadruply bonded. The possibilities for modification of this simple process are limitless only being restricted by the imagination and organic-inorganic synthetic skills of those skilled in the art of making HPMOs.

Additionally this process need not be limited to silica based framework materials. It can easily be extended to allow the modification of any type of mesoporous metal-oxide framework to which the silsesquioxane, or other type of "paint" precursors (hereafter referred to as guest molecules) will bind. This allows the guest molecules to be bound directly to materials that may have desirable electrical, or photochemical properties that are lacking in the silica based framework materials thereby increasing their utility. The guest molecules can include not only silsesquioxanes, but also any type of guest that will bind to the framework material via two or more linkages. These materials are exemplified by, but not limited to all manner of bis-phosphonates, bis-carboxylates and bis-sulphonates and combinations thereof.

In summary, the essence of the invention of HPMOs described herein is that one can use a low value periodic mesoporous silica of the type invented by

Mobil Corporation (MCM41 and MCM48) or University of California at Santa Barbara (SBA) and transform it in a single and straightforward step into a high value HPMO in which all of the desired bridging organic function is placed exactly where one needs it, namely exclusively on the surface of the channel walls. One  
5 can carry out the same procedure for a periodic mesoporous organosilica (PMO) to make a HPMO. These HPMOs are envisioned to be useful for applications aimed at exploiting for example the chemical and physical, mechanical and electrical, acoustical and optical properties of the bridging organic function.

Therefore it is clear that hybrid periodic mesoporous organosilicas,  
10 HPMOs, the subject of the invention described herein, are a new class of hybrid organic-inorganic mesoporous material, which are considered to be quite distinct to either the periodic mesoporous silica (MCM41 or MCM48 or SBA type) or periodic mesoporous organosilica (PMO) materials described above.

The present invention provides a method for producing a new class of  
15 nanocomposite materials we call hybrid periodic mesoporous organosilicas (HPMOs). This new class of materials consists of a porous metal oxide or a porous hybrid organic-inorganic framework material to which an organic, organometallic or biological guest molecule has been attached to the surface of the pores through two or more chemical linkages. The unusual combination of  
20 inorganic and organic chemical structure with this scale of porosity and surfaces suggests a myriad of uses for HPMOs, such as the controlled release and uptake of chemicals, chiral separations and catalysis, electronic printing and

microelectronic packaging, chemical sensing and bioassays, thermal and acoustic insulation.

5 The aforementioned framework materials should have pores in the size range of 2-30 nm. These pores can be well ordered and of uniform size, but this is not a requirement of this invention. Open frameworks with randomly oriented pores can work equally well. The organic, organometallic or biological guest molecules that are attached to the pore wall can be any molecules that contain two or more reactive groups that are capable of reacting with the surface of the metal oxide framework in such a way as to form chemical linkages and are  
10 capable of fitting into the pores. As example only, silsesquioxanes of the general formula  $(RO)_3Si-R'-Si(OR)_3$  can react with the pendant silanol groups of a porous silica framework to form two new Si-O-Si linkages between the silsesquioxane, and the framework.

15 This invention allows for the pore walls of the frameworks to be coated to varying extents by the organic, organometallic or biological molecules. By choosing the synthesis conditions carefully it is possible to completely cover the pore walls with a monolayer or to have only very sparse sub-monolayer coverage. By judicious selection of the guest molecules and anchoring chemistry it is also possible to produce multi-layers of either the same guest molecule or  
20 differing guest molecules and by means of which one can also control the wall thickness and enhance the mechanical stability of the materials.

The present invention provides a new material exemplified but not limited to a hybrid periodic mesoporous organosilica (HPMO). The material may be



prepared with a range of morphologies exemplified but not limited to, powder, free standing or supported film, patterned film, monolith, fiber, hollow cylinder, spirals or sphere forms.

5 The present invention provides a hybrid organic-inorganic mesoporous material comprising a mesoporous material having a porous framework and pre-selected organic, organometallic, or biological molecules chemically attached to a surface of the pores through two or more chemical linkages.

The present invention provides a method of synthesizing a hybrid organic-inorganic mesoporous material comprising the steps of:

10 chemically binding a pre-selected molecule to the pore walls of a pre-existing mesoporous material having a porous framework through two or more chemical linkages.

### BRIEF DESCRIPTION OF THE DRAWINGS

15 The method of producing new hybrid periodic mesoporous organosilicas in accordance with the present invention will now be described, by way of example only, reference being made to the accompanying drawings, in which:

Figure 1 illustrates the chemical structures of silsesquioxanes that were attached to the pore walls of PMS and PMO materials: (a) 20 bis(triethoxysilyl)methane; (b) 1,2-bis(triethoxysilyl)ethane; (c) 1,2-bis(triethoxysilyl)ethylene; (d) 1,6-bis(triethoxysilyl)hexane; (e) 2,5-bis(triethoxysilyl)-*p*-xylene; (f) *N,N*-bis[3-(triethoxysilyl)propyl]amine; and (g) 1,1-bis(trichlorosilylmethyl)ethylene.

Figure 2 shows the PXRD diffraction patterns of (a) a surfactant extracted PMS; and (b) surfactant extracted PMS that has been refluxed in toluene for 96 hours.

5 Figure 3 shows the powder X-ray diffraction (PXRD) patterns of (a) mesoporous silica refluxed in toluene for 96 h; (b) mesoporous silica treated with 1,6-bis(triethoxysilyl)hexane; (c) mesoporous silica treated with bis(triethoxysilyl)methane; and (d) mesoporous silica treated with N,N-bis(triethoxysilylpropyl)amine.

10 Figure 4 shows the  $^{13}\text{C}$  CPMAS NMR of: (a) a surfactant extracted PMS that has been treated with 1,2-bis(triethoxysilyl)ethane prior to the treatment in a basic solution; and (b) the same sample after treatment in a basic solution. The asterisks denote spinning side bands, and the peaks at 73 ppm are due to residual surfactant template.

15 Figure 5 shows the  $^{29}\text{Si}$  MAS NMR of template extracted mesoporous silica (a) prior to any treatment; (b) after treatment with 1,2-bis(triethoxysilyl)ethane; and (c) following treatment with a dilute ammonia solution.

20 Figure 6 shows  $^{13}\text{C}$  CPMAS NMR of: (a) a surfactant extracted PMS that has been treated with 1,2-bis(triethoxysilyl)ethene prior to the treatment in a basic solution; and (b) the same sample after treatment in a basic solution. The asterisks denote spinning side bands, and the peaks at 73 ppm are due to residual surfactant template.

Figure 7 shows the nitrogen adsorption isotherm of: (a) template extracted mesoporous silica that has been refluxed in toluene; and (b) mesoporous silica that has been treated with bis(triethoxysilyl)methane.

Figure 8 shows the nitrogen adsorption isotherms of: (a) template  
5 extracted mesoporous silica; (b) mesoporous silica that has been treated with 1,1-bis(trichlorosilylmethyl)ethylene once; and (c) mesoporous silica that has been treated with 1,1-bis(trichlorosilylmethyl)ethylene twice.

Figure 9 shows a schematic representation of the potential binding modes  
10 of a silsesquioxane to a PMS or PMO substrate in which the silsesquioxane could bind through both Si atoms as in the case of 1,2-bis(triethoxysilyl)ethane, or through only a single silicon atom as in the case of 2,5-bis(triethoxysilyl)-p-xylene.

Figure 10 shows the the T region of the  $^{29}\text{Si}$  MAS NMR spectrum of a PMS framework that has been treated with 2,5-bis(triethoxysilyl)-p-xylene.

15 Scheme 1: Shows a representation of the structures of five key structures: top left – a PMS in which the pore walls are made entirely of silica; top right - a PMO in which the pore walls are made up of organic bridge-bonded silica; middle - a PMS to which an organosilane containing a terminally bonded organic group has been anchored to the pore walls through only one chemical linkage; bottom  
20 left - a HPMO-1 in which a silsesquioxane containing a bridge bonded organic group has been anchored to a PMS framework through at least two chemical linkages; bottom right a HPMO-2 in which a silsesquioxane containing a bridge

bonded organic group has been bound to a PMO framework through at least two chemical linkages.

### DETAILED DESCRIPTION OF THE INVENTION

5           As used herein, the term "template" or "supramolecular template" means a self-aggregation of ionic or non-ionic molecules or polymers that have a structure directing function for another molecule or polymer.

          As used herein, the term "periodic mesoporous" means having an ordered arrangement of pores in terms of translation symmetry with a diameter between  
10       about 2 and about 30 nm.

          As used herein, the term "surfactant mesostructure" means an ordered supramolecular assembly of surfactant molecule micelles, with translation symmetry between about 2 and about 30 nm.

          As used herein, the term "framework material" means the mesoporous  
15       material to which the organic, organometallic or biological molecules are attached via two or more chemical linkages.

          As used herein, the term "guest molecule" means the organic, organometallic or biological molecule that is bound to the framework via two or more chemical linkages.

20           As used herein the term "HMPO I" means hybrid periodic mesoporous organo silica type I that consists of a periodic mesoporous silica (PMS) framework material that has had a silsesquioxane guest bound to its pore walls via two or more chemical linkages.

As used herein the term "HMPO II" means hybrid periodic mesoporous organo silica type II that consists of a periodic mesoporous organosilica (PMO) framework material that has had a silsesquioxane guest bound to its pore walls via two or more chemical linkages.

5           The present invention describes new composite materials, referred to as hybrid organic-inorganic mesoporous materials (HPMOs – HPMO I and HPMO II) in which organic, organometallic or biological guest molecules are chemically bound to a porous framework material through two or more chemical linkages.

10           For the purpose of demonstration only, periodic mesoporous silica (PMS) and periodic mesoporous organosilica (PMO) were chosen as the framework materials for the studies described herein. Additionally, silsesquioxanes of the general formula  $[(RO)_3Si]_2R'$  were chosen as the guest molecules because these materials exemplify the claims that are being made herein. These specific examples give rise to a subclass of materials termed hybrid periodic mesoporous organosilicas (HPMOs - classes HPMO I and HPMO II).

15           PMO and PMS materials with mesopore sizes of approximately 8 nm were synthesized using non-ionic surfactant templates using methods that have been previously described, specifically using Pluronic P123 as the supramolecular template, (see - Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. **Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 Angstrom pores** *Science*, 279, 548 (1998) and Burleigh, M. C.; Markowitz, M. A.; Wong, E. M.; Lin, J. S.; Gaber, B. P. **Synthesis of periodic mesoporous organosilicas with block copolymer**



templates *Chem. Mater.*, 13, 4411 (2001)). The template was then removed from these powders by washing exhaustively with 1:1 mixtures of acetone and diethylether.

A variety of silsesquioxanes were then attached to the pore walls of these templates. These silsesquioxanes include: bis(triethoxysilyl)methane; 1,2-bis(triethoxysilyl)ethane; 1,2-bis(triethoxysilyl)ethylene; 1,6-bis(triethoxysilyl)hexane; *N,N*-bis[3-(triethoxysilyl)propyl]amine; and 2,5-bis(triethoxysilyl)-*p*-xylene. The chlorosilane 1,1-bis(triethoxysilylmethyl)ethylene was also used (see Figure 1).

In the all of the studies presented herein here the supramolecular template was removed from the PMS or PMO prior to the addition of the silsesquioxane, however, it is also feasible to add the silsesquioxane directly to the as-synthesized template-containing PMS or PMO in a one step process whereby the silsesquioxane is able to simultaneously displace the imbibed template from the as-synthesized template-containing PMS or PMO and thereby anchor to silanol groups on the pore wall of the PMS or PMO through two or more chemical linkages.

### **Synthesis of HPMOs**

#### ***When using a silsesquioxane:***

In a typical synthesis 1.0 g of PMS was dried at 100 °C under vacuum for 24 hours and was then mixed with 75 mL of toluene. After stirring until the powder is well dispersed (approximately 30 min) 2.6 g (7.25 mmol) of 1,2-bis(triethoxysilyl)ethane was added to the mixture. This mixture was then heated

to reflux for 96 hours. The resulting powder was then isolated by vacuum filtration and washed several times with toluene, and then dried at 80°C for at least 6 hours. This powder was then dispersed in a dilute NH<sub>4</sub>OH solution for 24 hours in order to complete the hydrolysis of the ethoxysilyl groups. The powder was again isolated by vacuum filtration, washed with water and then dried at 100 °C.

Syntheses involving other silsesquioxanes or PMO templates were carried out analogously.

***When using a chlorosilane:***

In a typical synthesis 1.0 g of PMS was dried at 100 °C under vacuum for 24 hours and was then mixed with 75 mL of toluene. After stirring until the powder is well dispersed (approximately 30 min) 2.34 g (7.25 mmol) of 1,1-bis(trichlorosilylmethyl)ethylene was added to the mixture. This mixture was then heated to reflux for 96 hours. The resulting powder was then isolated by vacuum filtration and washed several times with toluene, and then dried at 80 °C for at least 6 hours. This powder was then dispersed in water for 24 hours in order to quench the residual chlorosilyl groups. The powder was again isolated by vacuum filtration, washed with water and then dried at 100 °C.

The above processes were also repeated on the same powder samples in order to add multi-layers to the pore walls.

Powder X-ray diffraction (PXRD) was used to confirm that the structure of the frameworks is retained in the treatments described above. Figure 2 shows the X-ray diffraction patterns of a PMS framework before and after it has been refluxed in toluene for 96 hours. The peak positions and intensities remain

constant indicating that the framework is not degraded. Figure 3 shows that the addition of the silsesquioxanes 1,6-bis(triethoxysilyl)hexane, bis(triethoxysilyl)methane, and N,N-bis(triethoxysilylpropyl)amine during reflux gives similar results, showing no degradation of the silica framework.

5           <sup>13</sup>C CPMAS NMR confirms that the silsesquioxanes bind to the framework material. Figure 4 shows the <sup>13</sup>C CPMAS NMR of a PMS framework that has been treated with 1,2-bis(triethoxysilyl)ethane both before treatment in a basic solution and after this treatment. In Figure 4a (before the powder has been treated in a basic solution) unhydrolyzed ethoxy groups cause the peaks at 57  
10 ppm and 17 ppm. After treatment in a basic solution, Figure 4b, these peaks are removed, confirming that hydrolysis is completed. The <sup>29</sup>Si MAS NMR spectra of these samples, shown in Figure 5, also confirm the addition of the silsesquioxane to the framework material. In Figure 5a, before the addition of the silsesquioxane, only Q sites are observed corresponding to the silica framework.  
15 In figure 5b, after treatment with 1,2-bis(triethoxysilyl)ethane, a strong signal can be seen in the T region of the spectrum, primarily corresponding to T1 (-70 ppm) and T2 (-77 ppm) signals, which results from the attachment of the silsesquioxane. After treatment in a basic solution, the T signals shift so that there are primarily T2 (-70 ppm) and T3 (-83 ppm) sites, indicating that the added  
20 silsesquioxanes condense further upon treatment.

Similar results are observed when a PMO framework synthesized from 1,2-bis(triethoxysilyl)ethane is treated with 1,2-bis(triethoxysilyl)ethylene as seen in Figure 6. In Figure 6a the <sup>13</sup>C CPMAS NMR of just the framework material is

shown, and the only peak observed is that of the ethane group. After treatment with 1,2-bis(triethoxysilyl)ethylene a peak can be seen at 145 ppm corresponding to the ethylene group, as well as peaks at 57 ppm and 17 ppm corresponding to unhydrolysed ethoxy groups (Figure 6b). After treatment in a basic solution the peaks from the ethoxy groups are no longer present (figure 6c), confirming that hydrolysis has been completed.

The porosity of the samples both before and after treatment with silsesquioxanes is confirmed by their nitrogen adsorption isotherms. Figure 7 shows the isotherms of a PMS framework both before (Figure 7a) and after (Figure 7b) treatment with bis(triethoxysilyl)methane. A significant decrease in pore volume can be seen in the treated sample. Similar results are observed when using a chlorosilane. Figure 8 shows the nitrogen adsorption isotherms of a PMS framework before any treatment (Figure 8a), after one treatment with 1,1-(bistrichlorosilylmethyl)ethylene (Figure 8b) and after two treatments with 1,1-(bistrichlorosilylmethyl)ethylene (Figure 8c). The pore volume can be seen to decrease with successive treatments. Additionally, the isotherms shift to lower pressures with successive treatments indicating decreasing pore sizes.

$^{29}\text{Si}$  MAS NMR can be used to verify that the silsesquioxane guest molecules do in fact bind to the PMS and PMO frameworks through two chemical linkages. If a PMS framework is treated with 2,5-bis(triethoxysilyl)-p-xylene then the rigidity of the aryl ring as well as the bulkiness of the methyl groups will prevent both silicon atoms from being able to bind to the framework, whereas when PMS is treated with 1,2-bis(triethoxysilyl)ethane both silicon atoms are able

to bind to the framework as shown in Figure 9.  $^{29}\text{Si}$  MAS NMR confirms these modes of binding. Figure 10 shows the T region of the  $^{29}\text{Si}$  MAS NMR of a PMS framework that has been treated with 2,5-bis(triethoxysilyl)-p-xylene. A strong signal in the T0 region (-61 ppm) can be seen which corresponds to the silicon atom that is not bound to the framework. In comparison, the  $^{29}\text{Si}$  MAS NMR of a PMS framework that has been treated with 1,2-bis(triethoxysilyl)ethane (Figure 5b) shows no signal in the T0 region indicating that both silicon atoms are bound to the framework. All other silsesquioxanes described herein were found to bind to the framework through both silicon atoms.

## Instrumentation

PXRD patterns were measured with a Siemens D5000 diffractometer using  $\text{Cu K}\alpha_1$ -radiation ( $\lambda = 154.18 \text{ pm}$ ). All solid state NMR experiments were performed with a Bruker DSX 400 NMR spectrometer.  $^{29}\text{Si}$  MAS-NMR spectra were recorded at a spin rate of 5 kHz and a pulse delay of 1 min.  $^{13}\text{C}$  CP MAS-NMR experiments were performed at a spin rate of 5 kHz, a contact time of 5 ms and a pulse delay of 3 s. Sorption experiments were performed by a Quantachrome Autosorb-1C machine with  $\text{N}_2$  as sorption gas at 77 K starting at a relative pressure  $p/p_0 = 10^{-5}$ . Seven data points were selected for BET analysis from relative pressure of 0.1. SEM images were recorded with a Hitachi S-4500 microscope at 1 kV without Au coating on the samples.

With the work presented herein we have demonstrated that silsesquioxanes of the general formula  $[(\text{RO})_3\text{Si}]_2\text{R}'$  can be chemically anchored to the walls of PMS frameworks (giving a sub-class of materials termed HPMO I)



and PMO frameworks (giving a subclass of materials termed HPMO II) in such a way that the organic bridging group is bound to the wall through at least two chemical linkages. This provides a facile method of anchoring any number of different silsesquioxanes to the pore walls. These silsesquioxanes, depending on their structure, may be capable of imparting new physical and chemical properties to the highly porous framework materials, including, but not limited to, changing the dielectric constant of the material, increasing its hardness, improving its mechanical, thermal or acoustical behavior, imparting catalytic activity, separating and sensing molecules or biomolecules, releasing at a controlled rate imbibed chemicals or pharmaceuticals, or the ability to scrub toxins from the environment. By anchoring ligands to the channel walls, the resulting HPMO could be made into an ideal support for transition metal catalysts. These possibilities, amongst others, make HPMOs useful for a wide variety of industrial applications.

In this work, pure PMS and PMO frameworks were used as examples to show the potential of this invention, but these are not the only conceivable platforms. For example, it is possible to produce PMO framework materials that contain several different organic bridging groups, or in which the organic groups are diluted with silica. The work described herein is applicable to all of these frameworks, regardless of their specific composition. Moreover it is not necessary that the frameworks be periodically ordered in the manner of the HPMOs described herein for this invention to apply. Aperiodic mesoporous frameworks will work equally well.

An obvious extension of this work is to include other types of mesoporous open framework materials that are not necessarily based around silica.

Mesoporous titania, as one example, has interesting electronic properties that could be exploited by chemically linking redox active molecules to the pore walls to be used for example in solar cells, electrochromic devices and photocatalysts.

Also anchoring molecules are not limited to silsesquioxanes with two or more chemical linking groups, they can also be multi-binding phosphonates, sulfonates, carboxylates to name a few.

The properties of the resulting hybrid organic-inorganic mesoporous material depend on the nature of the framework, the anchoring molecule, the template and structure type (e.g. MCM41, MCM48 and SBA type). Basic areas of application amongst others include microelectronics (low dielectric constant or low-*k* materials), separation techniques (e.g. chiral drug separation), bio-delivery, chemical storage (e.g. gas storage), catalysis, sensors, thermal and acoustic insulation.

It is to be emphasized that the HPMOs described in this invention are quite distinct to all of the known PMOs disclosed in both the patent and open literature. These distinctions are illustrated in Scheme 1. Specifically, all known PMOs reported prior to the disclosure of the HPMOs are synthesized in a process that involves the co-assembly of a silsesquioxane precursor and a surfactant or polymer template to create a PMO in which the organosilica material that comprises the pore wall is described as a homogeneous integrated matrix of the bridge bonded organic and silica constituents.

To be quite precise, the bridge bonded organic groups in the so-formed PMOs are located both on the surface of the pore walls and within the bulk regions of the pore walls. In stark contrast, the HPMOs disclosed herein are instead synthesized by a procedure that involves the chemical anchoring of a silsesquioxane, through two or more chemical linkages, to the silanol groups on the pore surface of a pre-existing periodic mesoporous silica PMS. Hence the disclosed HPMOs are clearly synthesized in a distinct way compared to all the known PMOs, to be precise the HPMOs are made by chemical grafting (anchoring, attachment, tethering) versus co-assembly for the PMOs, Furthermore the HPMOs represent a distinct class of materials compared to the PMOs because in the HPMOs the desired bridge bonded organic functionality is located exclusively on the surface of the pore walls and not in both the surface and bulk regions of the pore walls, which is a defining feature of the PMOs.

To further emphasize this difference, in the synthesis of the PMOs, the desired bridge bonded organic functionality has absolutely no option but to be located both on the surface and within the bulk regions of the pore walls. In the HPMOs the synthesis is intentionally designed to place the desired bridge bonded organic functionality exclusively on the surface of the pore walls with none within the bulk regions of the pore walls as found in the PMOs.

Previous studies have shown that terminally functionalized organosilicon reagents can be bound to the pore walls of PMS and PMO materials. However in these circumstances the organic groups are left dangling in the void of the pore and are not an integral part of the wall of the material, as shown in Scheme

1. In HPMOs on the other hand, the organic groups are bound to the pore walls through at least two chemical linkages, so that in the final material the organic group is a part of the wall.

5 All of the above is considered to represent a massive difference between the PMOs and HPMOs from the point of view of their synthesis and structure, where to repeat, in the HPMOs the bridge bonded organic groups are exclusively located on the pore wall surfaces whereas in the PMOs they are to be found both on the surface of the pore walls and in the bulk regions of the pore walls. This difference is especially important when it comes to designing and tailoring the chemical and physical properties, function and utility of the PMOs compared to the HPMOs.

Hence the HPMOs disclosed herein are (i) synthesized in a distinct way to the PMOs and (ii) are structurally distinct to the PMOs. This is the basis of the distinctiveness of HPMOs to PMOs.

15 As used herein, the terms, "comprises" and "comprising" are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms, "comprises" and "comprising" and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

20 The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of

the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.



**THEREFORE WHAT IS CLAIMED IS:**

1. A hybrid organic-inorganic mesoporous material comprising a mesoporous material having a porous framework and pre-selected organic, organometallic, or biological molecules chemically attached to a surface of the pores through two or more chemical linkages.
2. The material according to claim 1 in which the framework material is a mesoporous metal-oxide.
3. The material according to claim 1 in which the framework material is a mesoporous silica.
4. The material according to claim 1 in which the framework material is a mesoporous organosilica.
5. The material according to claim 3 in which the framework mesoporous silica is selected from the group consisting of MCM41, MCM48 and SBA type materials.

6. The material according to claim 2 in which the framework material is a mesoporous titania.
7. The material according to claims 1, 2, 3, 4, 5, or 6, in which the pore walls of the framework material are amorphous.
8. The material according to claims 1, 2, 4, or 6, in which the pore walls of the framework material are crystalline.
9. The material according to claims 1, 2, 4, or 6, in which the pore walls of the framework material are partially crystalline.
10. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, or 9, in which the pores are periodically ordered.
11. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, or 9, in which the pores are disordered.
12. A hybrid periodic mesoporous organosilica type I (HPMO I) comprising a mesoporous material having a periodic mesoporous silica (PMS) framework and

silsesquioxane molecules being chemically attached to the surface of the pores through two or more chemical linkages.

13. A hybrid periodic mesoporous organosilica type II (HPMO II) comprising a mesoporous material having a periodic mesoporous organosilica (PMO) framework having silsesquioxane guest molecules being chemically attached to the surface of the pores through two or more chemical linkages.

14. The material according to claims 4 or 13 wherein the framework material is synthesized using molecules selected from the group consisting of bis(triethoxysilyl)methane; 1,2-bis(triethoxysilyl)ethane, 1,2-bis(triethoxysilyl)ethylene; 1,4-bis(triethoxysilyl)benzene; 1,3-bis(triethoxysilyl)benzene; 1,3,5-tris(triethoxysilyl)benzene.

15. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14 in which the molecules are bound to the porous framework material by two or more chemical linkages.

16. The material according to claim 15 in which the pore walls of the framework material are partially covered by the molecules.

17. The material according to claim 15 in which the pore walls of the framework material are substantially completely covered by the molecules.
18. The material according to claims 15, 16, or 17 in which the molecules bound to the pore walls are a single type of molecule.
19. The material according to claims 15, 16, or 17 in which the molecules bound to the pore walls are of two or more different types of molecules.
20. The material according to claims 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 14, 15, 16, 17, 18, or 19 in which the linkages between the framework and the molecules are Si-O-Si linkages or Si-R-Si linkages.
21. The material according to claims 15, 16, 17, 18, or 19 in which the molecules are a silsesquioxane molecule.
22. The material according to claim 21 in which the silsesquioxane is selected from the group bis(triethoxysilyl)methane; 1,2-bis(triethoxysilyl)ethane; 1,2-bis(triethoxysilyl)ethylene; 1,6-bis(triethoxysilyl)hexane; *N,N*-bis[3-(triethoxysilyl)propyl]amine; 2,5-bis(triethoxysilyl)-*p*-xylene, and 1,1-bis(triethoxysilylmethyl)ethylene.

23. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, or 22 formed as a powder.
24. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, or 22 formed as a film.
25. The material according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, or 22 formed as a monolith.
26. A method of synthesizing a hybrid organic-inorganic mesoporous material comprising the steps of:
- chemically binding a pre-selected molecule to the pore walls of a pre-existing mesoporous material having a porous framework through two or more chemical linkages.
27. The method according to claims 26 wherein the pre-existing mesoporous material is a periodic mesoporous material.
28. A method of synthesizing a hybrid organic-inorganic mesoporous material comprising the steps of:

removing a supramolecular template from a pre-existing mesoporous material having a porous framework; and

chemically binding a pre-selected molecule to the pore walls of the mesoporous material through two or more chemical linkages.

29. The method according to claims 28 wherein the pre-existing mesoporous material is a periodic mesoporous material.

30. A method of synthesizing a hybrid organic-inorganic material comprising the steps of:

synthesizing a mesoporous material having a porous framework using a suitable supramolecular template; and

chemically binding a molecule to the surface of the pore walls.

31. The method according to claims 30 wherein the pre-existing mesoporous material is a periodic mesoporous material.

32. A method of synthesizing a hybrid organic-inorganic material comprising the steps of:

synthesizing a mesoporous material having a porous framework using a suitable supramolecular template;

removing the supramolecular template; and



chemically binding a pre-selected molecule to the surface of the pore walls.

33. The method according to claims 32 wherein the pre-existing mesoporous material is a periodic mesoporous material.

34. A method of synthesizing a hybrid mesoporous organosilica (HPMO) comprising the steps of:

synthesizing a mesoporous silica (PMS) having pores using a suitable supramolecular template; and

chemically binding a pre-selected molecule to the surface of the pore walls.

35. The method according to claims 34 wherein the mesoporous silica (PMS) is a periodic mesoporous silica (PMS).

36. A method of synthesizing a hybrid mesoporous organosilica (HPMO) comprising the steps of:

synthesizing a mesoporous silica (PMS), or periodic mesoporous organosilica (PMO) having pores using a suitable supramolecular template; removing the supramolecular template; and

chemically binding a pre-selected molecule to the surface of the pore walls through two or more chemical linkages.

37. The method according to claims 36 wherein the mesoporous silica (PMS) is a periodic mesoporous silica (PMS).

38. A method of synthesizing a hybrid mesoporous silica (HPMO) comprising the steps of:

chemically binding a pre-selected molecule to silanol groups located on pore walls of a pre-existing mesoporous silica through two or more chemical linkages.

39. The method according to claims 38 wherein the mesoporous silica is a periodic mesoporous silica.

40. The method according to claims 26, 27, 28, 29, 30, 31, 32, 33, 34, 36, 37, 38 or 39 wherein the molecule is a silsesquioxane.

41. The method according to claims 40 wherein the silsesquioxane is selected from the group consisting of 1,2-bis(triethoxysilyl)methane; 1,2-bis(triethoxysilyl)ethane; 1,2-bis(triethoxysilyl)ethylene; 1,6-

bis(triethoxysilyl)hexane; *N,N*-bis[3-(triethoxysilyl)propyl]amine; 2,5-bis(triethoxysilyl)-*p*-xylene, and 1,1-bis(triethoxysilylmethyl)ethylene.

42. The method according to claim 26, 27, 28, 29, 30, 31, 32, 33, 34, 36, 37, 38 or 39 wherein the molecule has the general formula  $[(RO)_3Si]_nR'$  with  $n \geq 2$  and  $R'$  is a bridging organic, organometallic or biological group.

43. A method of synthesizing a hybrid periodic mesoporous silica (HPMO) comprising the steps of:

removing a supramolecular template from a pre-existing periodic mesoporous silica; and

chemically binding a silsesquioxane guest molecule to silanol groups located on pore walls through two or more chemical linkages.

44. A method of synthesizing a hybrid periodic mesoporous silica (HPMO) comprising the steps of:

chemically binding a silsesquioxane molecule to silanol groups located on pore walls of a pre-existing periodic periodic mesoporous organosilica through two or more chemical linkages.

45. A method of synthesizing a hybrid periodic mesoporous silica (HPMO) comprising the steps of:

removing a supramolecular template from a pre-existing periodic mesoporous organosilica; and

chemically binding preselected molecules to silanol groups located on pore walls through two or more chemical linkages.

46. The method according to claim 26 to 45 wherein the supramolecular template is selected to give pore sizes in a range from about 2 nm to about 30 nm.

47. The method according to claim 26 to 46 39 formed as a powder.

48. The method according to claim 26 to 46 formed as a film.

49. The method according to claim 26 to 46 formed as a monolith.

## ABSTRACT

The present invention provides a synthetic strategy for creating a new class of materials called hybrid organic-inorganic mesoporous materials, exemplified but not limited to hybrid periodic mesoporous organosilicas (HPMOs). This strategy involves taking a pre-assembled mesoporous material having a porous framework and then attaching an organic, inorganic or biological guest molecule to the pore walls of the framework material through two or more chemical linkages. The unusual combination of inorganic and organic components organized into a material with mesoscale porosity and having bridge bonded organic, organometallic, or biological functionalized surfaces suggests a myriad of uses for these composite materials, such as the controlled release and uptake of chemicals, chiral separations and catalysis, electronic printing and microelectronic packaging, thermal and acoustical insulation.

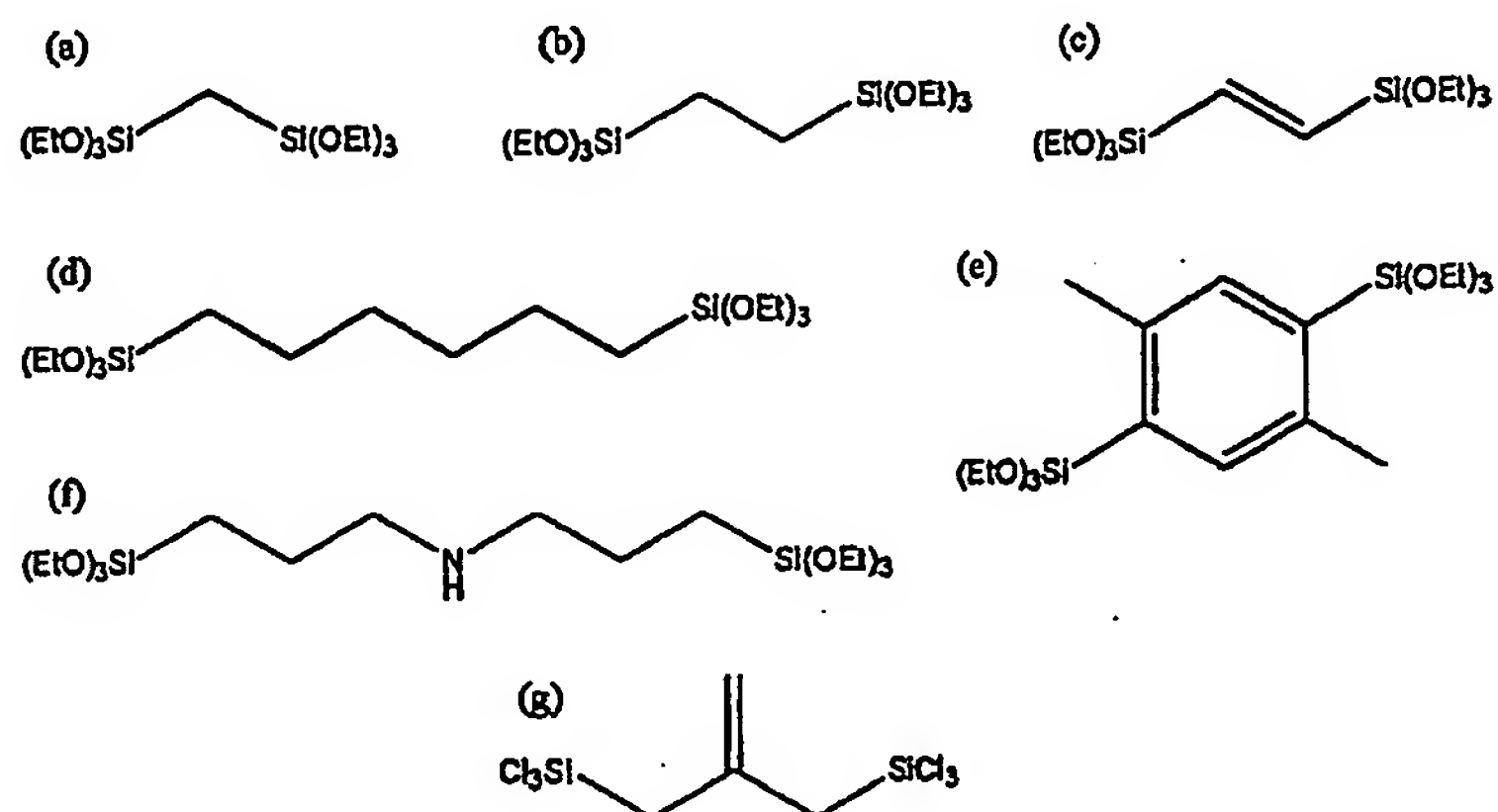


Figure 1: Chemical structures of silsesquioxanes that were attached to the pore walls of PMS and PMO materials: (a) bis(triethoxysilyl)methane; (b) 1,2-bis(triethoxysilyl)ethane; (c) 1,2-bis(triethoxysilyl)ethylene; (d) 1,6-bis(triethoxysilyl)hexane; (e) 2,5-bis(triethoxysilyl)-p-xylene; (f) N,N-bis[3-(triethoxysilyl)propyl]amine; (g) 1,1-bis(trichlorosilylmethyl)ethylene.



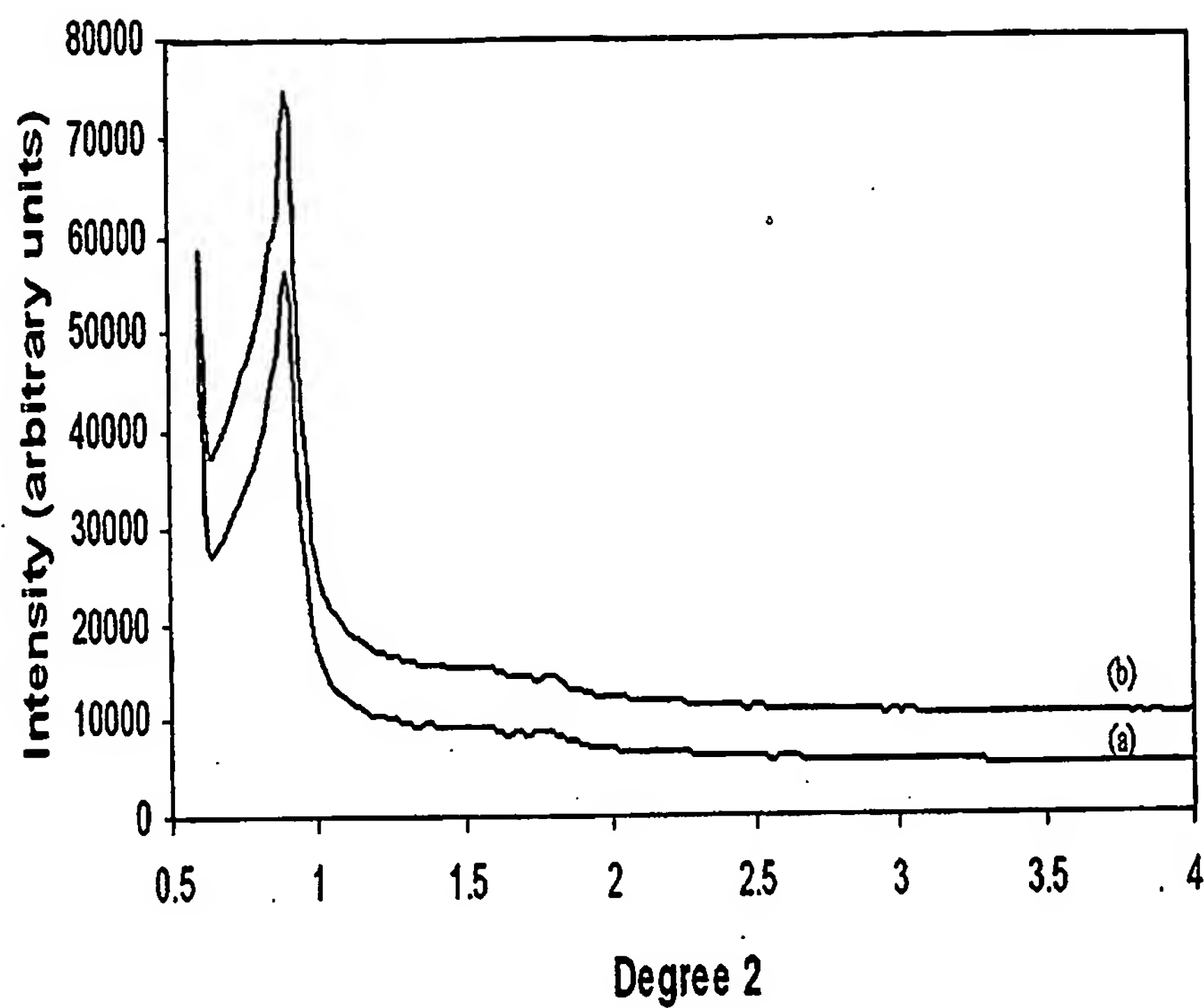


Figure 2: PXRD diffraction patterns of (a) extracted PMS; and (b) surfactant extracted PMS that has been refluxed in toluene for 96 hours.

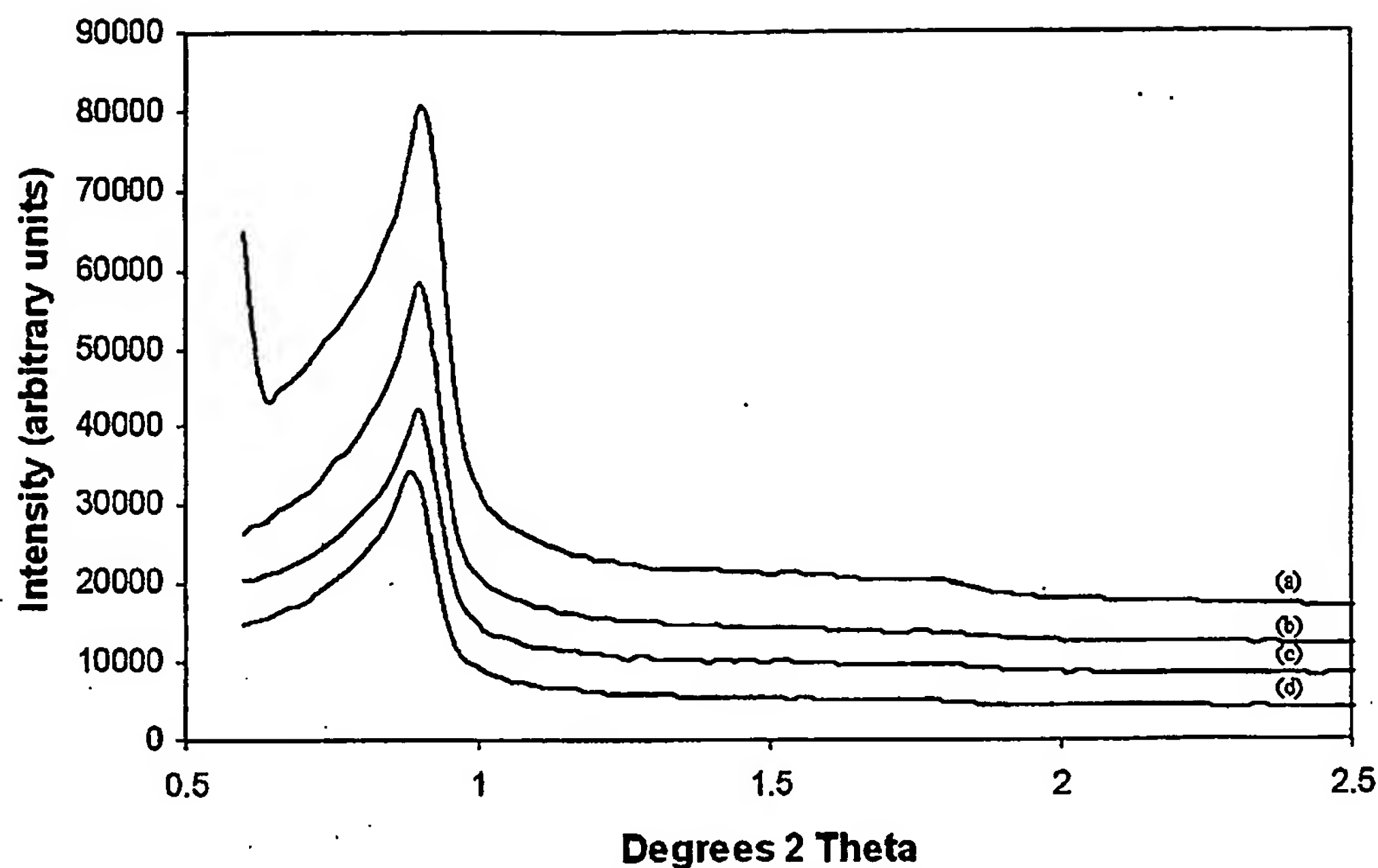


Figure 3: Powder X-ray diffraction (PXRD) pattern of (a) mesoporous silica refluxed in toluene for 96 h; (b) mesoporous silica treated with 1,6-bis(triethoxysilyl)hexane; (c) mesoporous silica treated with bis(triethoxysilyl)methane; and (d) mesoporous silica treated with N,N-bis(triethoxysilylpropyl)amine.

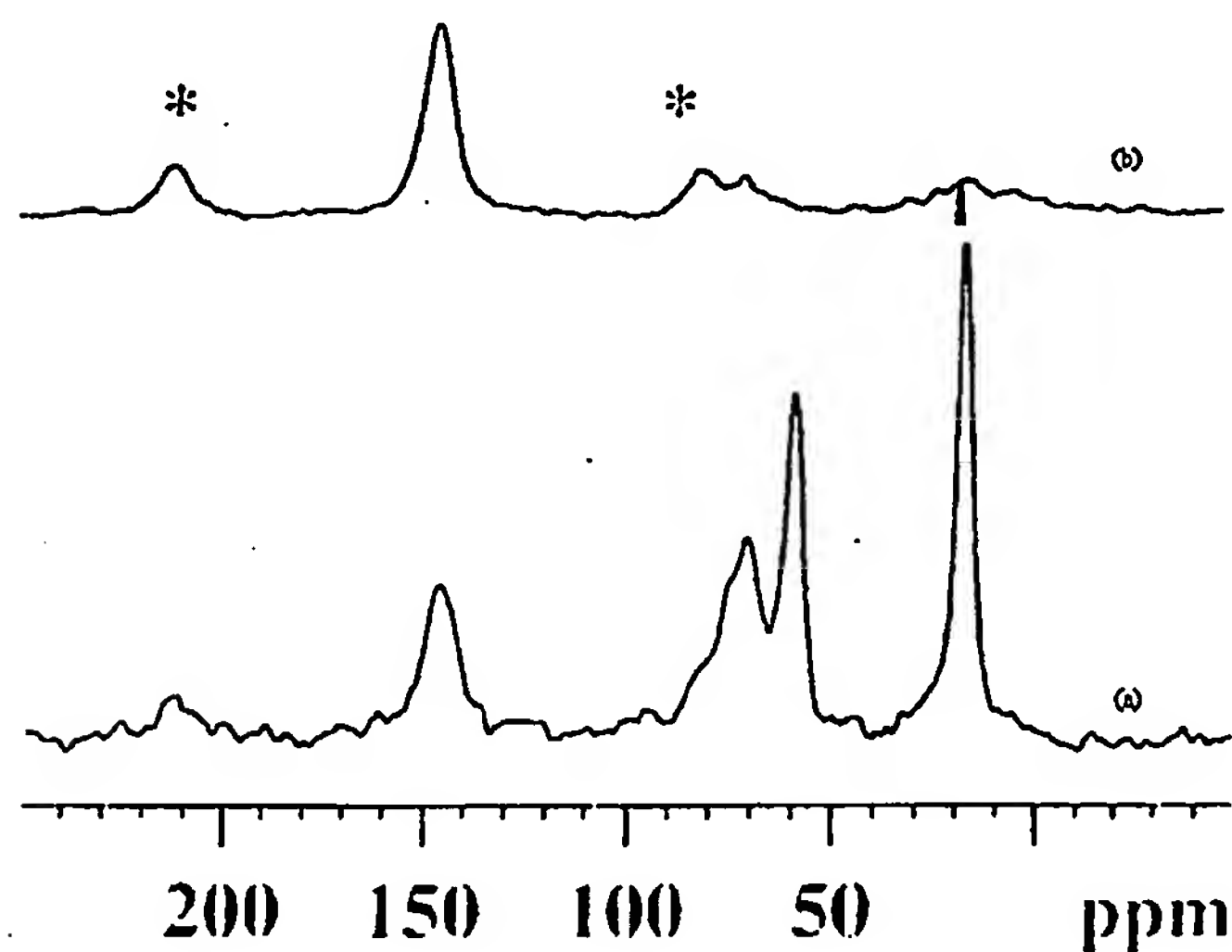


Figure 4:  $^{13}\text{C}$  CPMAS NMR of: (a) PMS that has been treated with 1,2-bis(triethoxysilyl)ethane prior to the treatment in a basic solution; and (b) the same sample after treatment in a basic solution. The asterisks denote spinning side bands, and the peaks at 73 ppm are due to residual surfactant template.

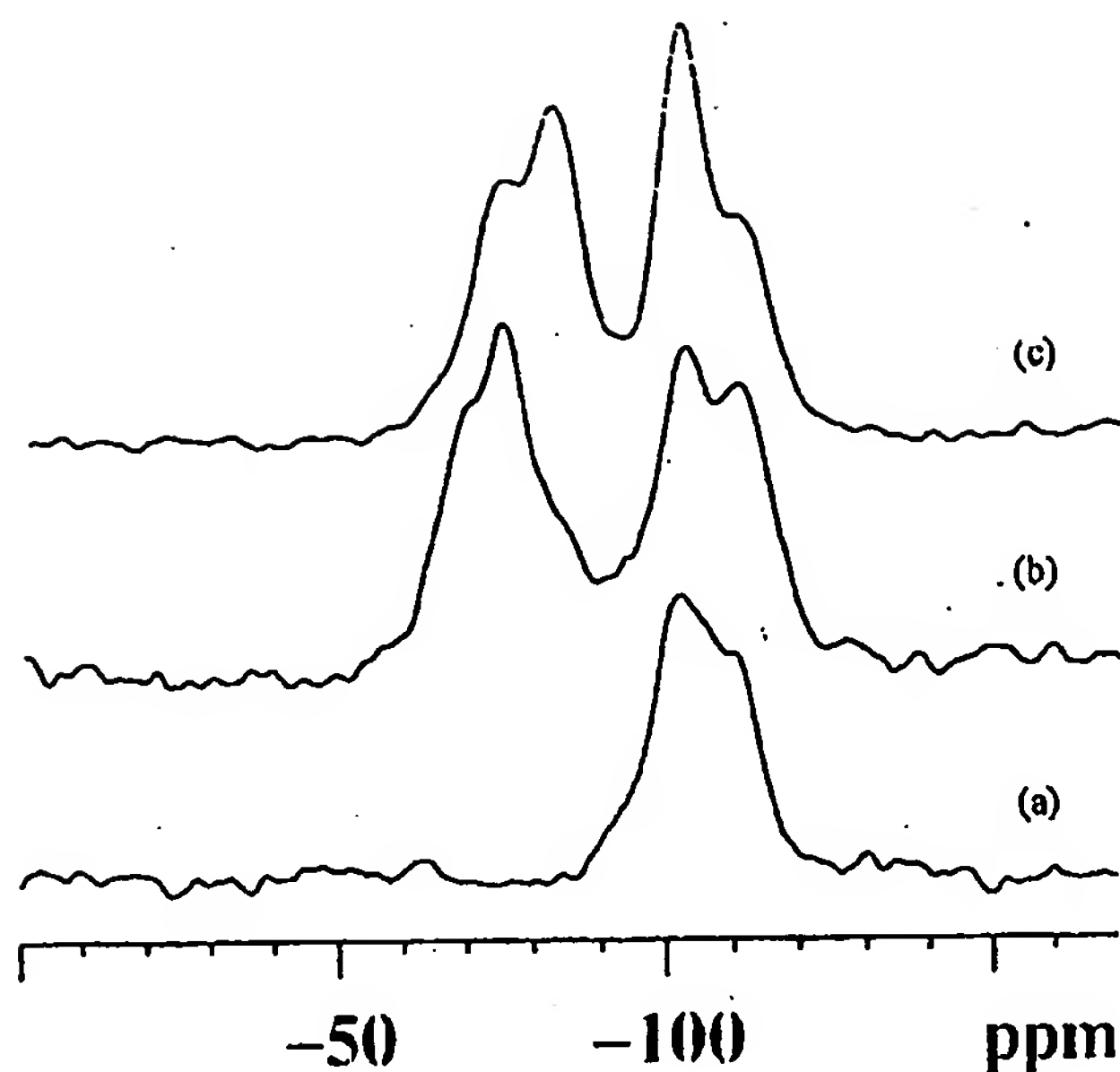


Figure 5:  $^{29}\text{Si}$  MAS NMR of template extracted mesoporous silica (a) prior to any treatment; (b) after treatment with 1,2-bis(triethoxysilyl)ethane; and (c) following treatment with a dilute ammonia solution.

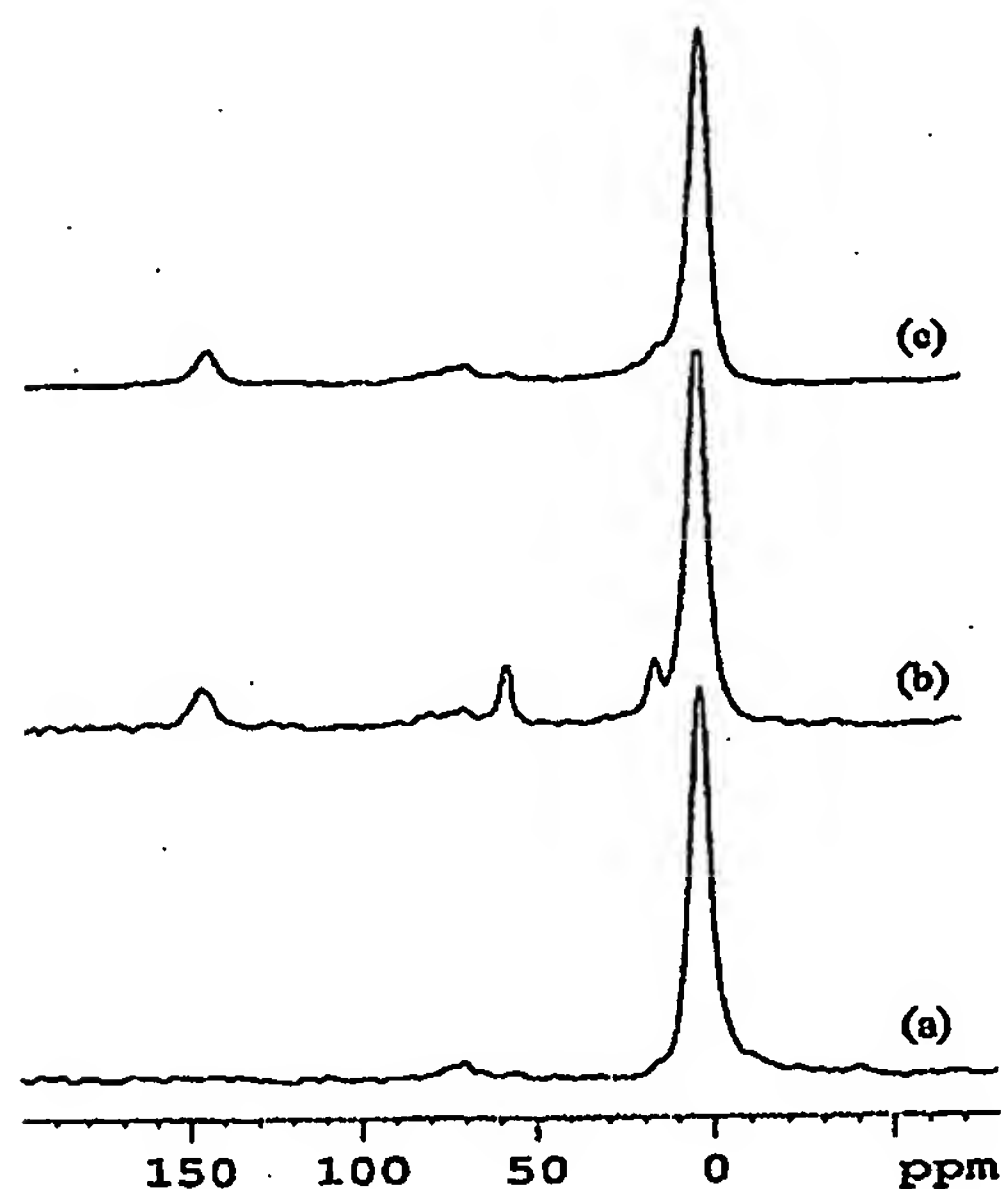


Figure 6:  $^{13}\text{C}$  CPMAS NMR of: (a) a PMO framework made from 1,2-bis(triethoxysilyl)ethane; (b) the same PMO framework that has been treated with 1,2-bis(triethoxysilyl)ethylene prior to treatment in a basic solution; and (c) after treatment in a basic solution.

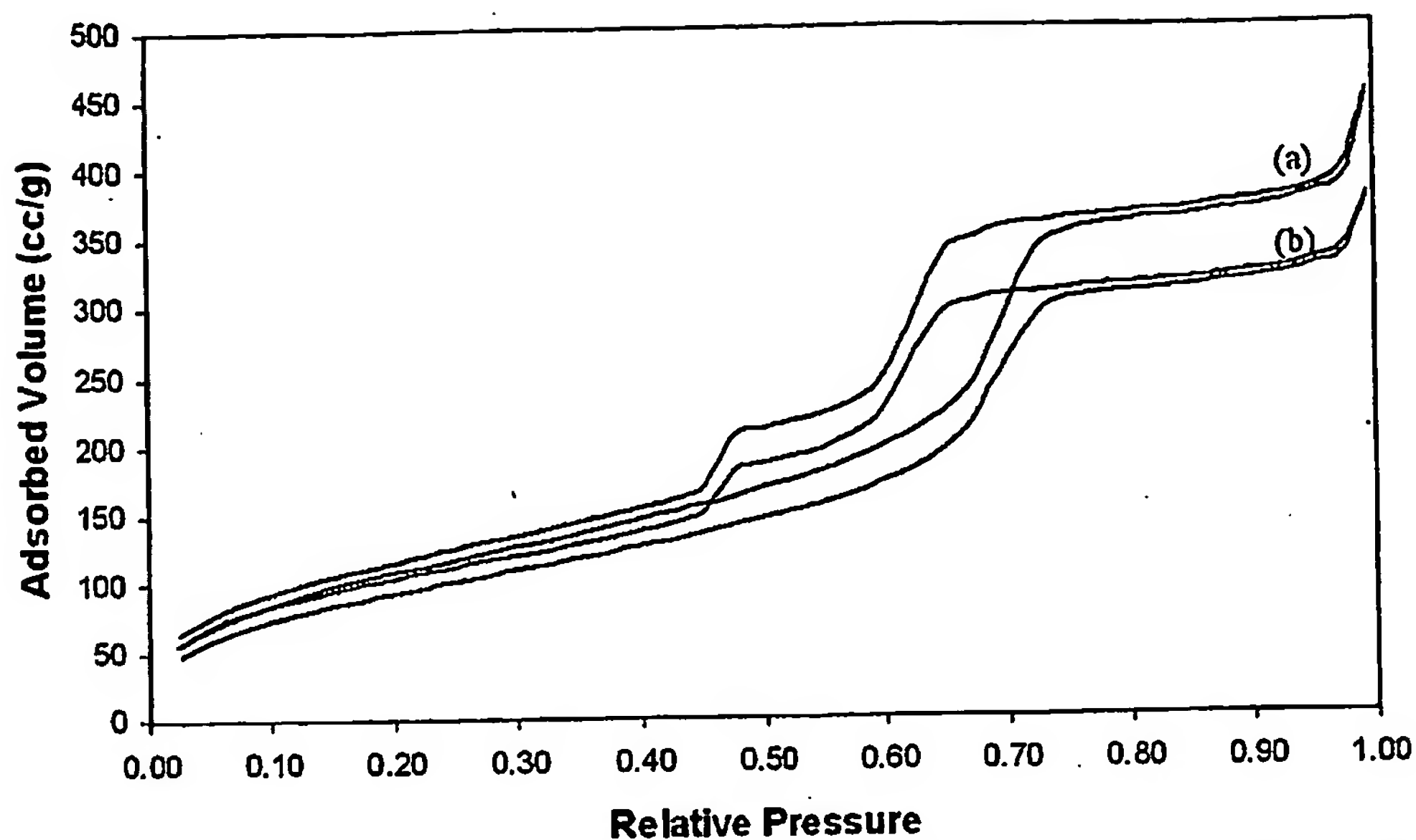


Figure 7: Nitrogen adsorption isotherm of: (a) template extracted mesoporous silica that has been refluxed in toluene; and (b) mesoporous silica that has been treated with bis(triethoxysilyl)methane.

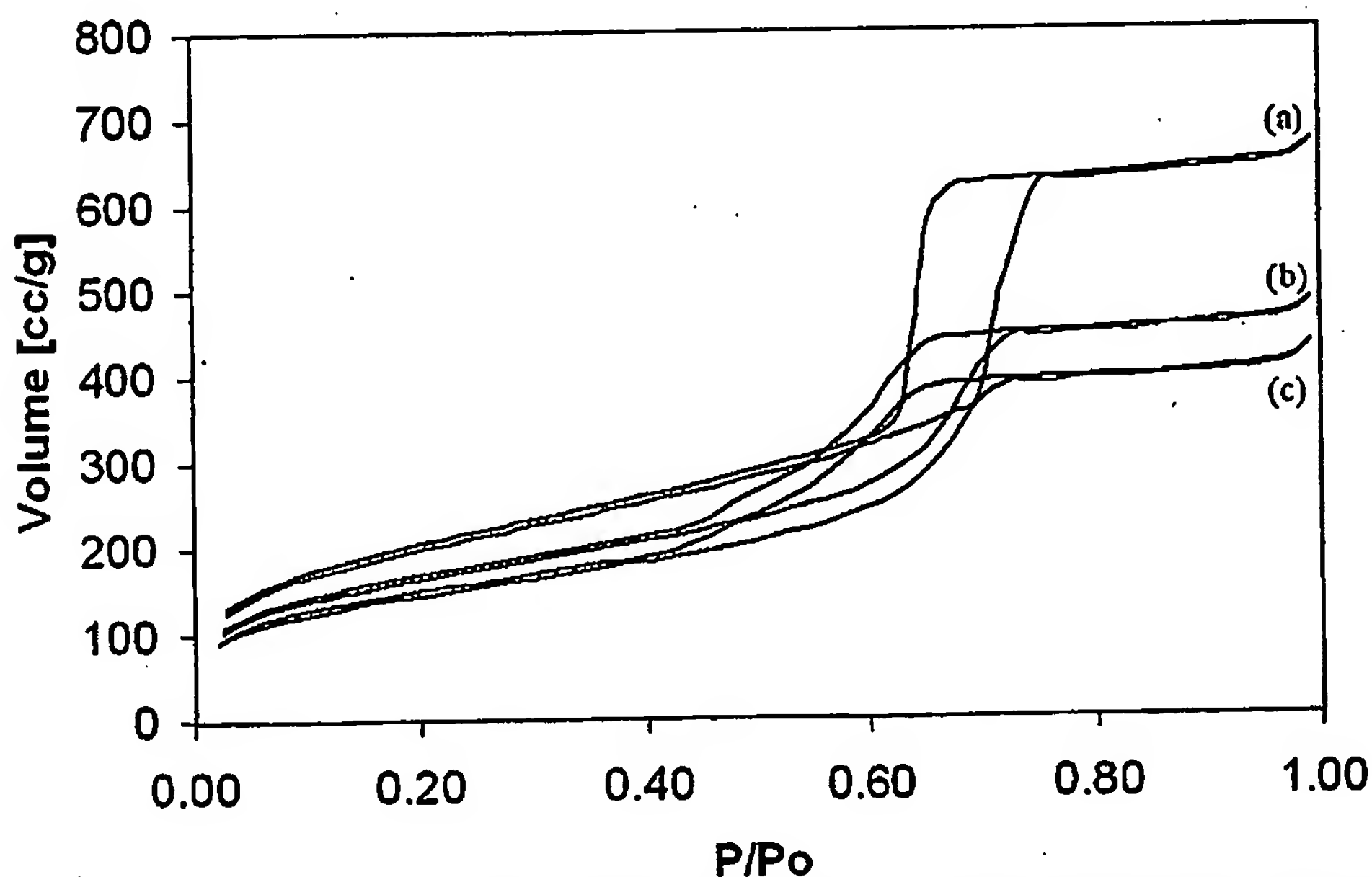


Figure 8: Nitrogen adsorption isotherms of: (a) template extracted mesoporous silica; (b) mesoporous silica that has been treated with 1,1-bis(trichlorosilylmethyl)ethylene once; and (c) mesoporous silica that has been treated with 1,1-bis(trichlorosilylmethyl)ethylene twice.

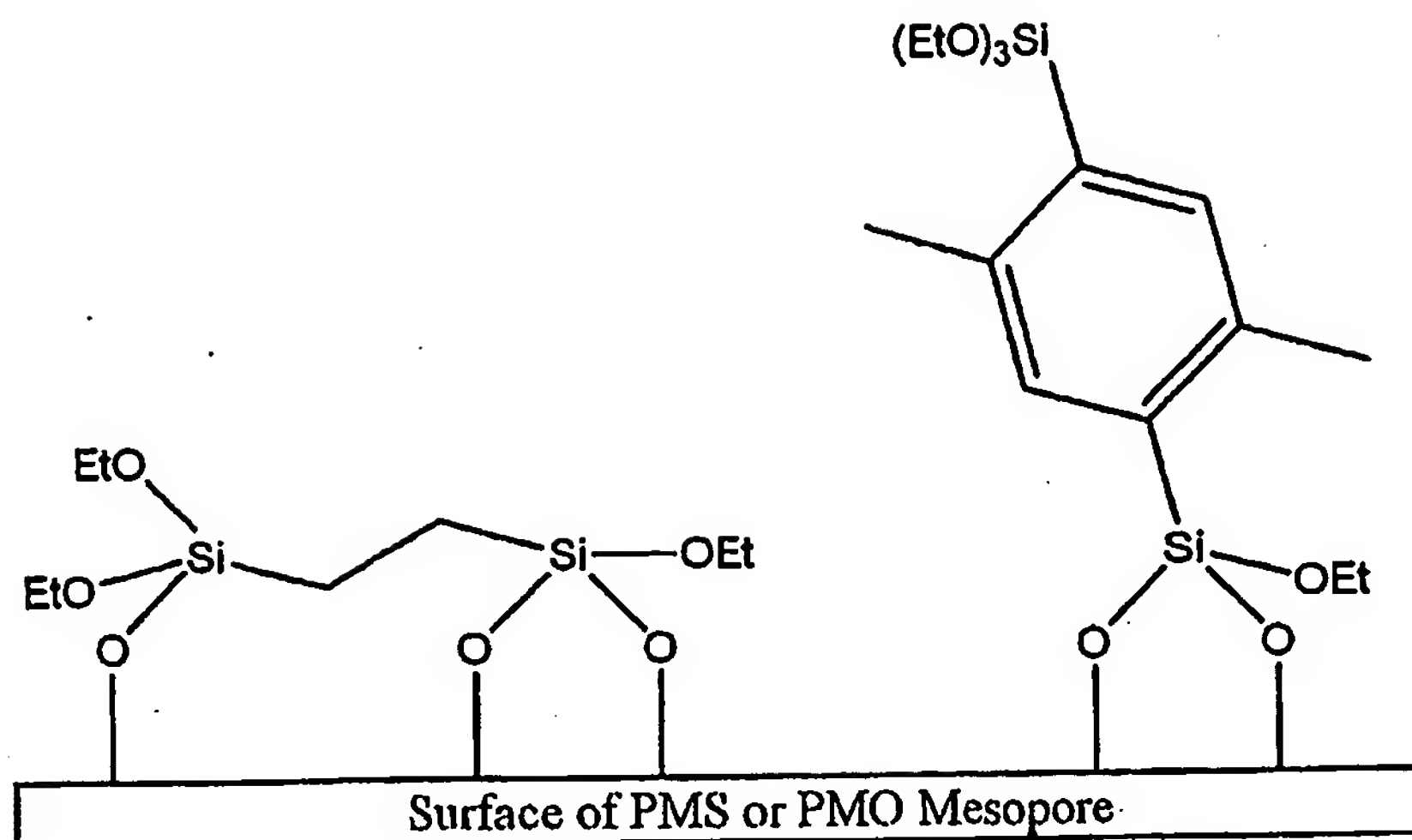


Figure 9: Schematic representation of potential binding modes of a silsesquioxane to a PMS or PMO substrate. The silsesquioxane could bind through both Si atoms as in the case of 1,2-bis(triethoxysilyl)ethane (left), or through only a single silicon atom as in the case of 2,5-bis(triethoxysilyl)-p-xylene (right).

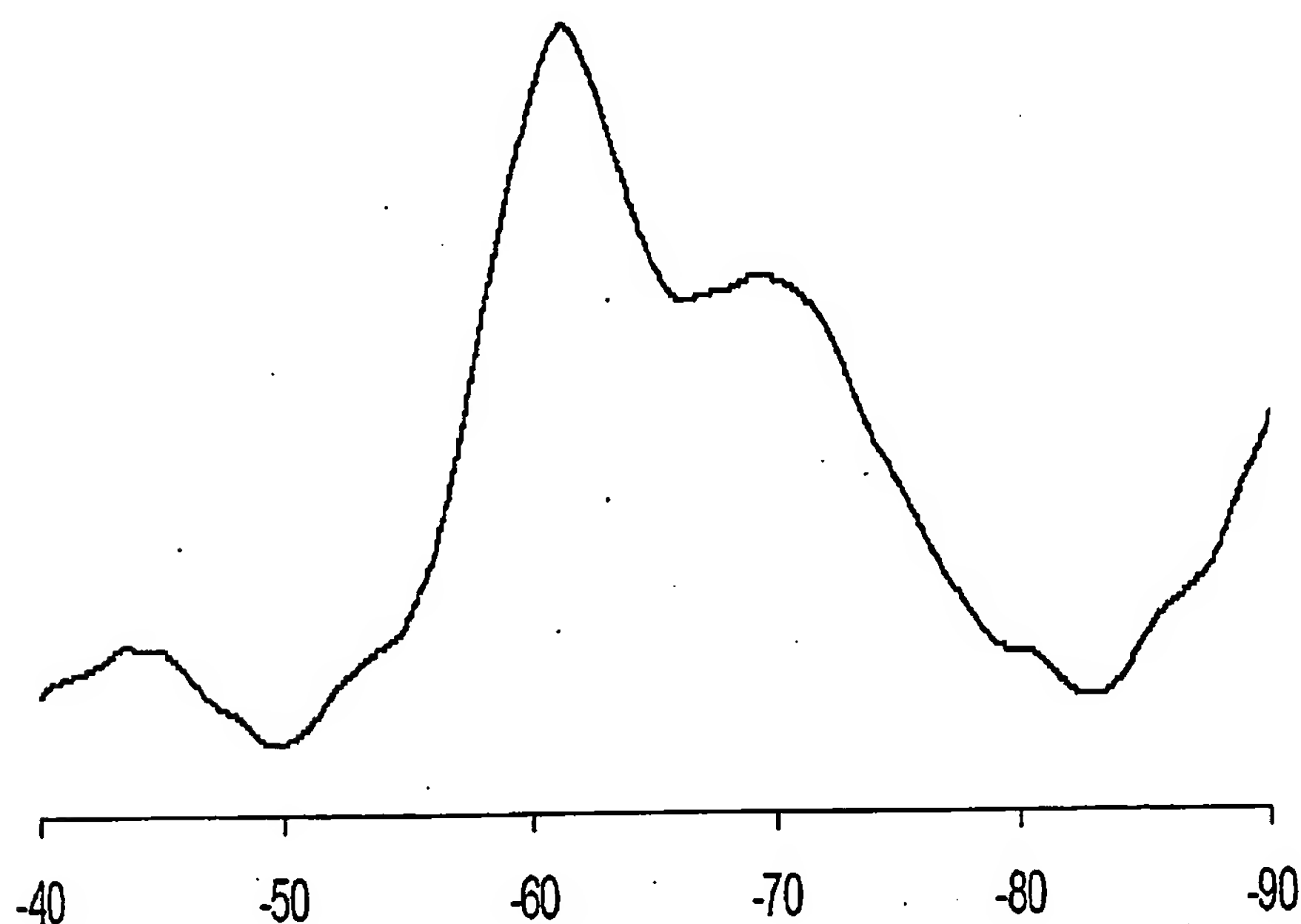
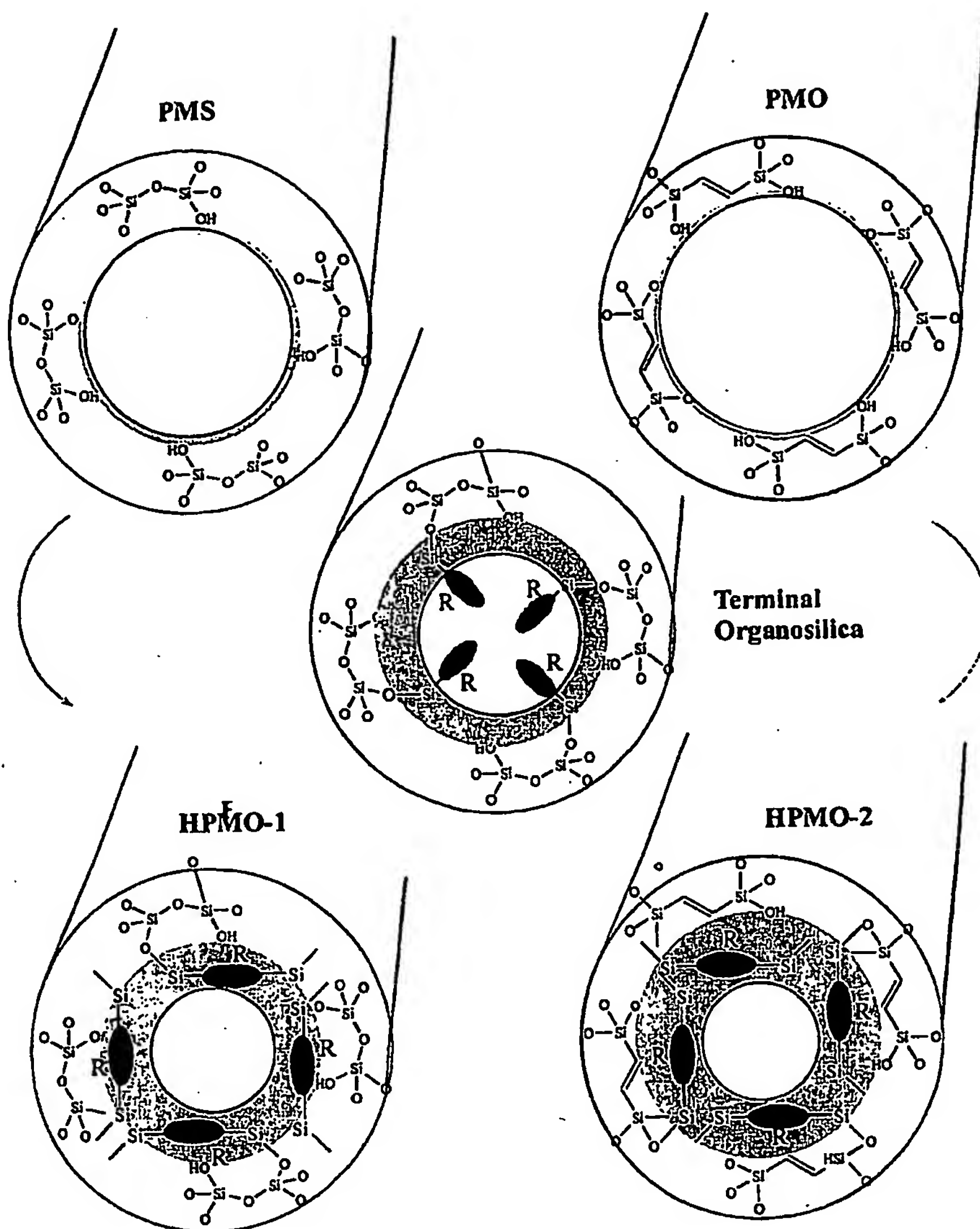


Figure 10:  $^{29}\text{Si}$  MAS NMR spectrum of the T region of a PMS framework that has been treated with 2,5-bis(triethoxysilyl)-p-xylene.



**Scheme 1:** Shows a representation of the structures of five key structures: top left – a PMS in which the pore walls are made entirely of silica; top right - a PMO in which the pore walls are made up of organic bridge-bonded silica; middle - a PMS to which an organosilane containing a terminally bonded organic group has been anchored to the pore walls through only one chemical linkage; bottom left - a HPMO-1 in which a silsesquioxane containing a bridge bonded organic group has been anchored to a PMS framework through at least two chemical linkages; bottom right a HPMO-2 in which a silsesquioxane containing a bridge bonded organic group has been bound to a PMO framework through at least two chemical linkages.



From the INTERNATIONAL BUREAU

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Date of mailing (day/month/year) 03 May 2005 (03.05.2005)	
Applicant's or agent's file reference 101060P	<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/CA05/000406	International filing date (day/month/year) 16 March 2005 (16.03.2005)
International publication date (day/month/year)	Priority date (day/month/year) 16 March 2004 (16.03.2004)
Applicant THE GOVERNING COUNCIL OF THE UNIVERSITY OF TORONTO et al	

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<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
16 March 2004 (16.03.2004)	60/553,121	US	27 April 2005 (27.04.2005)

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